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One-pot Synthesis of Glycidyl Nitrate

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Abstract: A mild, low cost synthetic method of glycidyl nitrate is developed via so called one-pot procedure. Epichlorohydrin added dropwise to the dilute nitric acid (35 wt%) resulted in ring-opening reaction at about 20 ℃. Ring-closing occurred then by the addition of aqueous sodium hydroxide. Glycidyl nitrate was obtained in moderate yield (60%) and its structure was characterized by Fourier transform infrared spectroscopy, hydrogen and carbon nuclear magnetic resonance and elemental analysis.

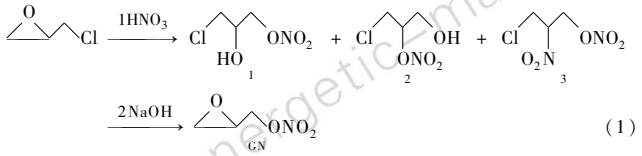
Key words: organic chemistry; energetic material; synthesis; glycidyl nitrate; one-pot synthesis

CLC number: TJ55; O623.624 **Document code**: A

1 Introduction

Glycidyl nitrate (GN) is the monomer of poly glycidyl nitrate (PGN), which is a hydroxyl terminated, energetic, poly-isocyanate curable polyether for propellant, explosive and pyrotechnics development[1]. General synthesis of GN included two-step procedure of ring-opening of epichlorohydrin (ECH) by nitrate agents and ring-closing by strong base[2~4]. Highsmith et al[5,6] prepared GN via the nitration of glycerol using concentrated nitric acid (90 wt%) and the cyclization of dinitroglycerin using sodium hydroxide. Unfortunately, significant amount of nitroglycerine (NG) and dinitroglycerine (DNG) remained in the reaction mixture.

In this study, GN synthesized via one-pot synthesis route were shownd in reaction (1), using dilute 35 wt% nitric acid.



(1)

2 Experimental

2.1 General

All reagents and organic solvents were of analytical grade without further purification. Fourier transform infrared (FT-IR) spectra were recorded for neat samples with Nicolet-60SXR-FTIR (USA) spectrometer. ^{1}H and ^{13}C NMR spectra were recorded with INOVA-400 spectrometer. $CDCl_3$ was used as solvent, and tetramethylsilane (TMS) as internal standard. Purity of GN was confirmed by GC-930 (Shanghai, China). Microanalyses were performed by the EA 1112 microanalysis center (GERMAN).

2.2 Synthesis of GN

H_2O (180 mL) was added to a three-neck flask and cooled to below 5 ℃. Nitric acid (270 mL, 63 wt%) was added dropwise while keeping the inner temperature below 7 ℃. The nitric acid aqueous solution (~35 wt%) was stirred for an additional 30 min at 5~7 ℃. ECH (200 g) was added dropwise to the nitric acid solution over a period of 60 min, while keeping the inner temperature at ~20 ℃. After adding ECH, the solution was stirred for an additional 180 min at ~20 ℃. Then the solution was cooled to below 5 ℃ and aqueous sodium hydroxide (180 g in 200 mL H_2O) was added dropwise over a period of 60 min. The system temperature rose gradually while adding sodium hydroxide solution. The reaction solution was stirred for an additional 120 min. Organic layer was separated and distilled at 59~61 ℃/1 000 Pa. The distillation was washed with water (200 mL ×3) and stored in the presence of 4A molecular mesh. GN (154 g (60%)) was obtained and the gas chromatography (GC) purity was >94%, n_D^{20} 1.4389.

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3 Results and discussion

Nitrate esters are usually prepared from corresponding alcohols by reaction with common nitrating agents such as mixtures of nitric acid and sulphuric acid, nitric acid and acetic anhydride, nitric acid with trifluoroacetic anhydride, or pure nitric acid alone[7]. Nitration using mixed acids or pure nitric acid is generally exothermic reaction, in other words, special precautions to prevent thermal runaway are required. And products separation is often a problem due to contamination of the organic product by residual acid, and this necessitates additional clean-up steps to ensure stability of the products.

Recently, some other routes from alcohols to nitrate esters have been developed. For example, ceric ammonium nitrate (CAN)[8] and silica-bond iron ion (Ⅲ) chloride ($FeCl_3/SiO_2$)[9] would act as an efficient catalyst for the ring-opening reaction of different epoxides to form corresponding nitrate esters. Dinitrogen pentoxide (N_2O_5) could cause the ring-opening nitration of epoxides and provide the corresponding nitrate esters cleanly and efficiently[10]. Desai et al[1] have developed a flow nitration method of glycidol using N_2O_5 and produced GN without further purification for polymerization.

Such methods suffer from several shortcomings. GN synthesized by the metal ions catalysts would associate with the metal ions that could interfere with the polymerization of GN. In N_2O_5 procedure, substitution of epoxide with electro-withdrawing and/or sterically bulky groups slows down the reaction and N_2O_5 is not commercially available[10].

The nitration products probably include 1,2 and 3 as shown in reaction (1), and 1 is the main product from ring-opening reaction of ECH using nitric acid. Kubota et al[11] studied the influence of concentration of nitric acid on the yield of 1. The results suggested that rapid rate and high amount of 2 and 3 were got while the concentration of nitric acid was >60 wt%. And sufficient cooling must be provided and more by-products,2,3 and their derivates in ring-closing reaction, would combined with GN. Impurities would prevent the polymerization of GN from forming PGN.

Moderate yield was obtained when nitration was carried out under mild conditions with dilute nitric acid alone 35 wt% and cyclization by adding sodium hydroxide solution directly to the reaction system.

The inner temperature would influence the yield of GN dramatically. When the ring-opening reaction was operated at below 5℃, the yield of GN would range between 7% and 15%.

GN is soluble in water, so too many times washing is harmful to the yield of GN. We choose a two-step post-process to separate GN from the reaction system. First, crude GN was distillated from the organic phase, and the second step is purification by water-washing.

The distillation would accompany some by-products,2,3,unreacted ECH, epoxide and oxirane derivated products and others. Fortunately, most of the by-products could be got rid of by water-washing. Nevertheless, there are still 6% by-products proved in GN by GC approximately.

The components are identified by elemental analysis, FTIR, ^{1}H NMR and ^{13}C NMR spectrum. The elemental analysis shows a good agreement between the calculated values and the measured values of GN. Elemental analysis data is shown as follows.

Elem. Ana. found: C,30.20; H,4.18; N,11.84; Calcd. for $C_3H_5NO_4$: C,30.26; H,4.23; N,11.76.

Fig. 1 shows FTIR spectrum of GN. The bands at 3491 cm^{-1} and 1052 cm^{-1} could be attributed to hydroxyl group. Combining with GC purity result, the impurities in GN probably are ring-opening products containing hydroxyl group. Bands at 3070 ~ 2985 cm^{-1} could be attributed to the CH_2 and CH groups. The 1637 and 1283 cm^{-1} bands could be assigned to asymmetric and symmetric NO_2 stretching mode respectively. Epoxide ether absorption could be observed at 859 cm^{-1}.

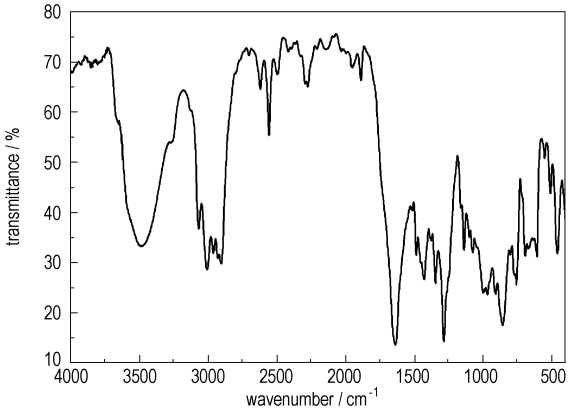

Fig. 1 FTIR spectrum of GN

Fig. 2. shows the ^{1}H-NMR spectrum of GN. The signal at $\delta = 3.28$ indicates the presence of ring C—H group, and the signal of ring C—H group of ECH is at $\delta = 3.25$. Comparing with the signals at $\delta = 2.91$ and 2.69 of the ring CH_2 group of ECH, the multiple peaks at $\delta = 2.91$ and 2.74 indicate the ring CH_2 group of GN. CH_2 group connecting $—ONO_2$ group shifts from double peaks at $\delta = 3.58$ of ECH and splits into two components at $\delta = 4.77$ and 4.33 of GN. It is probably caused by electro-withdrawing effect and stereochemistry of $—ONO_2$ group. Two weak signals at $\delta = 3.16$ and 2.81 could be assigned to impurities.

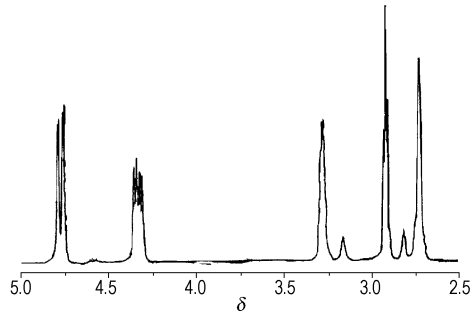

Fig. 2　^{1}H NMR spectrum of GN

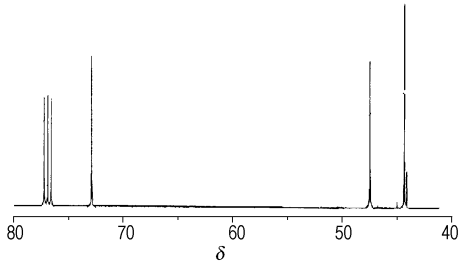

Fig. 3　^{13}C NMR spectrum of GN

The ^{13}CNMR spectrum of GN is shown in Fig. 3. Three signals at $\delta = 44.98$, 46.79 and 51.13 of ECH indicate the presence of —CH group, ring $—CH_2$ group and $—CH_2$ group connecting —Cl group, respectively. CH group and ring — CH_2 group of GN are observed at same regions, which appear at $\delta = 44.99$ and 47.48 respectively. In the region of $—CH_2ONO_2$, a down-field shift signal appears at $\delta = 73.02$. It is also contributed to the electro-withdrawing effect and stereochemistry of $—ONO_2$ group. The signals at $\delta = 77.00$, 77.20 and 77.32 are the characteristics of $CDCl_3$.

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缩水甘油硝酸酯的一锅法合成

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摘要: 环氧氯丙烷滴加到 35% 的稀硝酸中, 于 20 ℃左右进行开环反应, 然后用氢氧化钠溶液进行关环反应, 得到缩水甘油硝酸酯, 得率为 60%。用 FTIR, ^{1}H NMR, ^{13}C NMR 和元素分析对产物进行了结构表征。

关键词: 有机化学; 含能材料; 合成; 缩水甘油硝酸酯; 一锅法

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